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BOOK OF PAPERS

1996 International Conference & Exhibition



September 15-18
Opryland Hotel
Nashville, Tenn.

American Association of
Textile Chemists and Colorists

MODIFYING WOOL/COTTON TEXTILES FOR UNION DYEING

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Introduction

The escalating demand for comfortable and resilient all-seasonal apparel, especially in the casual-wear market, has sparked a renewed interest in wool/cotton blends. The lack of availability of these textiles is due in part to the difficulty in dyeing them to union shades. Current union dyeing processes rely on one or two dyebaths with one or two dyes. Although union shades for 80% cotton / 20% wool can be achieved with one dye in one dyebath, union shades in blends with higher wool content are difficult to achieve. In this case, cotton is dyed first under alkaline conditions with a reactive dye and then wool is dyed with an acid dye under acidic conditions at higher temperature. In the end there is final shade correction. The prevailing problem in dyeing wool in the presence of cotton is preferential dye uptake by wool. Recent reports described pretreating wool/cotton blends with resin/amine and resin/quaternary nitrogen compounds and with certain commercial dye fixatives before dyeing (1,2,3). Some of the fixatives contained reactive centers for modifying cellulose. All fixatives were polymeric and contained chain extensions with polyamino and/or quaternary ammonium functionality. These compounds aminized or cationized cotton so that cotton dyed similarly to wool with anionic dyes under acidic conditions and with wool-reactive dyes at nearly neutral pH. There were advantages and disadvantages to both pretreatment systems. Resin/amine and resin/quaternary nitrogen compounds exhibited good fiber permeation but less than easy processing by pad/dry/cure. Polymeric fixatives exhibited limited fiber penetration but easier processing by cold batching. Both pretreatment systems provided expedient routes to union dyeing.

This report summarizes and compares these systems:

1. N-Hydroxy- and N-methyl urea resins applied with a simple amine or quaternary compound, and
2. Fiber-reactive epoxide, azetidinium, and guanidino dye fixatives containing chain extensions with amine and/or quaternary ammonium functions.

Past investigations showed that:

- Resin/amine (MEA) pretreatments provided superior colorfastness in fabrics dyed with the wool reactive dye, C.I. Reactive Blue 69 (1).
- Resin/quaternary ammonium (choline chloride, CC) pretreatments for union dyeing wool/cotton with C.I. Acid Red 114 resulted in fabrics requiring the "dry clean only" label (2).
- Dye fixative pretreatments for union dyeing wool/cotton with C.I. Acid Red 114 led to unacceptable colorfastness to wet crocking and wash fastness staining (3).

We have re-examined the epoxy, azetidinium, and guanidine dye fixatives as pretreatments for union dyeing wool/cotton with C.I. Direct Red 79, and with the three wool reactive dyes: C.I. Reactive Red 65, C.I. Reactive Blue 69, and C.I. Reactive Yellow 39. We show now that the guanidine fixative yields union shades with acceptable colorfastness, provided wool-reactive dyes are used.

Experimental

Materials

Wool/cotton union cloth with worsted wool warp and pima cotton weft yarns (TF4504), cotton fabrics (TF400U print cloth and 400M mercerized), and wool fabrics (TF5400 woolen flannel, and TF530 nonchlorinated worsted wool challis) were obtained from Testfabrics, Inc.^a, Middlesex, NJ). The union cloth (Testfabrics, Inc.) was 62% worsted wool / 38% cotton of fabric count 48x44 and 2/42s worsted wool warp yarns interlaced with 40s/2 combed cotton yarns.

N-Hydroxy- and *N*-methyl urea resins were formulated as conventional dimethyloldihydroxyethyleneurea (DMDHEU), the capped form for low formaldehyde release (DMDHEU-G, glycolated), and the methylated form (4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone, DHDMI). DHDMI has methyl groups in place of methylol groups and thus it has zero-formaldehyde release. All resins were obtained from Freedom Textile Chemicals, Charlotte, NC.

The nitrogen-containing compounds, ethanolamine (MEA) (Aldrich, 141-43-51) and choline chloride (Du Pont/Con Agra, Verona, MO), were co-added to the resin baths.

The commercial dye fixatives contained various reactive centers: Freetex 670, cationic nitrogen (Freedom); Solfix E, epoxy (Ciba); Levogen FSE, azetidinium (Bayer), and Sandene 8425 Liquid cyanoguanidine (Clariant).

The resins and modified resins were applied as 13.6% to-15.0% on the weight of the fabrics (owf). They were coapplied with ethanolamine (MEA) as 7.8% to 11.7 % owf. These constituents were reacted *in situ* with wool/cotton union fabric, and in some cases to cotton and to wool by pad/dry/cure. The fabric was dried at 135C for 5 minutes and cured at 141C for 1 minute according to Cardamone, et al (1). These fabrics were dyed at pH 6.5 with C.I. Reactive Blue 69 (alpha-bromoacrylamido reactive group) as prescribed for this reactive dye.

Resin/CC, 4%/6% owf, was reacted *in situ* by the same procedure, dried at 125C for one minute, then cured at 160C for three minutes as reported by Cardamone et al. (2). These fabrics were dyed with C.I. Acid Red 114, C.I. Direct Red 79 under acidic conditions and C.I. Reactive Red 2 (dichlorotriazinyl), or C.I. Reactive Blue 19 (vinyl sulfone) under either acidic or neutral dyeing conditions for ionic or covalent bonding.

Dye fixatives were obtained as 30% to 55% solids. Fixative baths contained 20% of the original solution and were formulated on a liquor ratio of 30:1. Dyeing assistants included 10% Glauber's salt, 10%, ammonium sulfate, and Albegal B, an amphoteric wool leveling agent. The baths were adjusted to pH 11 with sodium hydroxide and the fabrics remained in the pretreatment baths for three hours at room temperature. They were subsequently dyed with C.I. Acid Red 114, or C.I. Direct Red 79 under acidic conditions and with C.I. Reactive Red 65, C.I. Reactive Blue 69, or C.I. Reactive Yellow 39 (all alpha-bromoacrylamido dyes) at pH 6.5. Reactive dyeings proceeded at a 20:1 liquor ratio according to the protocol established by the manufacturer: primary exhaustion over 60 minutes, followed by temperature rise to the boil for the final 60 minutes of dyeing. In the case of reactive dyeing, this procedure was followed by aftertreatment with sodium bicarbonate applied at pH 8.0-8.5 for 15 minutes at 80C-85C.

The effectiveness of a pretreatment was determined from the dyed fabric's color strength, K/S, obtained from a BYK-Gardner color measurement system that is used to measure the reflectance of dyed fabrics. In the Kubelka-Munk equation, $K/S = (1-R)/2R$, K/S is directly related to the color intensity of the fabric, where K is the light absorption coefficient, S is the light scattering coefficient, and R is the reflectance factor. Measurements of K/S for union dyed wool/cotton fabrics were compared to the K/S values of wool and cotton fabrics before and after pretreatment.

"Goodness" of union shade was determined from the digital images of the dyed fabrics. These digital images were displayed as histograms of pixel intensity over a 1 to 256 (black to white) gray-scale range. The images had been video-captured by an image analysis system configured with a solid state charge-coupled device (CCD) camera, a personal computer with a black/white frame-grabber board, and dedicated software. The standard deviation, S, of the histogram represented a fabric's uniformity of shade. Small values indicated union shade. Bimodal histograms contributed to a large S value and were characteristic of union fabric of which the two sets of interlacing yarns (warp and weft) were different shades (4,5).

Pretreatment Applications

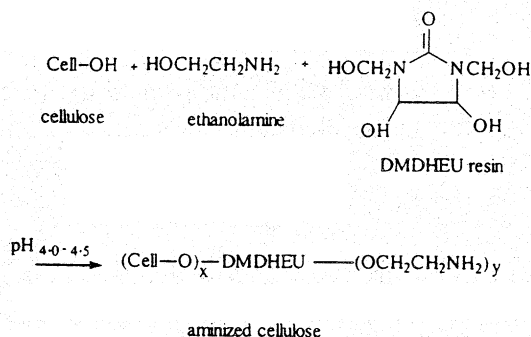
Pad/Dry/Cure

Reports originating from the textile chemistry research at the USDA ARS Southern Regional Research Center (SRRC), indicated that the amino derivatives of cellulose were prepared to induce ion-exchange capacity and to facilitate dyeing with wool dyes (6-11). In addition, cotton was modified with cationic character for differential color effects and for ease of dyeing with any anionic dye. These works provided the basis for our research on union dyeing wool/cotton blends.

In the union dyeing of wool/cotton blends, we examined two approaches:

1. Aminization

The crosslinking reactions of DMDHEU, DMDHEU-G, and DHDMI with cotton cellulose in the presence of MEA are shown below:



In the crosslinking reaction the resin was envisioned as forming a bridge between cellulose and the amine. The number of reactive sites was four for DMDHEU, two or four for DMDHEU-G, and two for DHDMI. In the case of DHDMI, there was little crosslinking (1). The results of union dyeing aminized wool/cotton from the pretreatments of these resins are found in Table 1.

Table 1: Effects of Resins and Modified Resins with MEA on the Dyeing of Wool/Cotton Union Cloth with C.I. Reactive Blue 69 (1).

Resin	% Dyeing	% Resin/ % MEA	K/S	S
1. DMDHEU	1	13.6/0	2.23	41.4
2. DMDHEU	1	13.6/7.8	4.97	25.4
3. DMDHEU-G	1	13.6/0	2.10	40.7
4. DMDHEU-G	0.3	13.6/7.8	2.40	22.6
5. DMDHEU-G	1	13.6/7.8	8.10	16.1
6. DMDHEU-G	2	13.6/7.8	16.8	18.0
7. DMDHEU-G	3	13.6/9.8	19.0	11.6
8. DHDMI	1	15.0/0	2.28	40.8
9. DHDMI	1	15.0/7.8	8.67	15.9
10. DHDMI	0.3	15.0/7.8	2.70	15.9

Without pretreatment, the K/S values of the dyed fabrics were low. The histograms of these dyed fabrics were bimodal and the S values were high. Note that DMDHEU/MEA was relatively ineffective for conveying high color strength when compared to DMDHEU-G and DHDMI. It could be reasoned that the high activity of DMDHEU involved more crosslinking to cellulose and thus limited reaction with MEA. DMDHEU-G provides a full range of union shades, 0.3% to 3.0%, with higher K/S and lower S values. DHDMI exhibited limited reactivity as suspected. Higher amounts of this resin could not compensate for low reactivity. Thus union shades with DHDMI/MEA were limited to 0.3% and 1% dyeings. Table 2 lists the results of colorfastness testing.

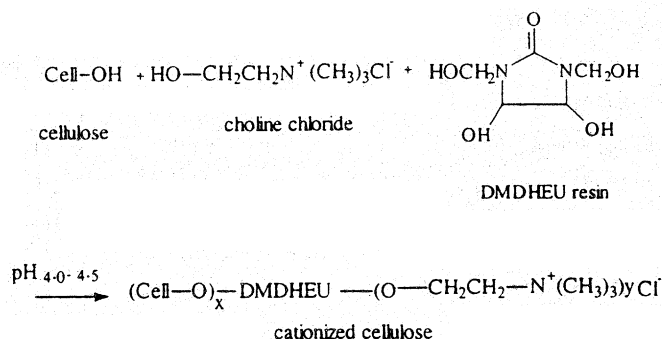
Table 2: Colorfastness of Wool/Cotton Pretreated with Resins/MEA before Dyeing with C.I. Reactive Blue 69.

Resin MEA	Croaking		Dry- clean	Color Change	Stain	Light 40 hr
	wet	dry				
DMDHEU	5	5	5	5	5	5
DMDHEU-G	5	5	5	5	5	5
DMDHEU-G	5	5	5	5	5	5
DMDHEU-G	5	5	5	5	5	5
DMDHEU-G.	5	5	5	5	5	5
DHDMI.	5	5	5	5	5	5
DHDMI.	5	5	5	5	5	5

Colorfastness was determined according to the standard test methods: AATCC Test Method 61 - Colorfastness to Laundering, Home and Commercial: Accelerated (Conditions IIA); AATCC Test Method 8 - Colorfastness to Crocking, Crockmeter Method (wet and dry conditions); AATCC Test Method 132 - Colorfastness to Dry Cleaning; and AATCC Test Method 16E - Colorfastness to Light. The effect on the color was determined by reference to the Gray Scale for Color Change, where a rating of 5 indicated negligible or no color change and ratings of 4 to 1 indicated a color change equivalent to Gray Scale Steps 4 to 1 (12).

2. Cationization

The crosslinking reaction of DMDHEU, DMDHEU-G, and DHDMI with cotton cellulose in the presence of choline chloride is shown below:



Wool/cotton and wool were pretreated with resin/CC at the SRRC laboratory. The dyes used in this pilot study were C.I. Acid Red 114, C.I. Direct Red 79, C.I. Reactive Red 2, and C.I. Reactive Blue 19 (Table 3).

Table 3: Effects of Resins/CC on the Dyeing of Wool Fabric and Wool/Cotton Union Cloth with C.I. Acid Red 114, C.I. Direct Red 79, C.I. Reactive Red 2, and C.I. Reactive Blue 19 at 3% owf.

Dye	% Resin/CC	K/S	S
<i>Wool (TF530)</i>			
C.I. Acid Red 114	0/0	29.9	7.2
C.I. Acid Red 114	4/6	27.6	7.5
C.I. Direct Red 79	0/0	28.2	6.6
C.I. Direct Red 79	4/6	26.6	6.7
C.I. Reactive Red 2	0/0	22.8	8.7
C.I. Reactive Red 2, acidic	4/6	22.1	8.4
C.I. Reactive Red 2, basic	4/6	11.6	10.0
C.I. Reactive Blue 19	0	26.1	5.7
C.I. Reactive Blue 19, acidic	4/6	24.9	5.4
C.I. Reactive Blue 19, basic	4/6	20.5	5.8
<i>Cotton/Wool (TF4504)</i>			
C.I. Acid Red 114	0/0	5.30	43.4
C.I. Acid Red 114	4/6	23.4	6.5
C.I. Direct Red 79	0	5.29	41.6
C.I. Direct Red 79	4/6	22.6	9.4
C.I. Reactive Red 2	0/0	5.29	43.6
C.I. Reactive Red 2, acidic	4/6	21.8	8.7
C.I. Reactive Red 2, basic	4/6	15.2	9.6
C.I. Reactive Blue 19	none	2.86	46.7
C.I. Reactive Blue 19, acidic	4/6	18.8	9.4
C.I. Reactive Blue 19, basic	4/6	17.6	9.3

It is clear from Table 3 that the depth of dyeing of wool in anionic dyeing was approximately the same with or without pretreatment. When, however, the reactive dyes were processed for covalent attachment in alkaline medium, there was a decrease in dye uptake on wool. Obviously, there is more attraction of the anionic dye for wool when wool was in its protonated form. Wool/cotton, on the other hand, exhibited dramatic dye uptake as the result of the pretreatment. Note that in the dyeings with C.I. Acid Red 114 and C.I. Direct Red 79, there was a slight reduction in depth of shade. This was more pronounced in the dyeings with C.I. Reactive Blue 19. In all dyeings, union shades were obtained for the pretreated fabrics as noted by the low S values.

Subsequently, a more complete study of resin/CC pretreatments and their effects on union dyeing wool/cotton was completed. Wool, wool/cotton and cotton fabrics were pretreated with DMDHEU, DMEHEU-G, and DHDMI, all with co-additive CC, at the SRRC laboratory. They were dyed at the ERRC laboratory and evaluated there for color strength, union shade, and colorfastness. Results are found in Table 4, where all fabrics listed were true union shades as evaluated objectively by image analysis.

Table 4: Effects of Resins/CC (4%/6%) Dyeings of Wool and Cotton and the Union Dyeings of Wool/Cotton Fabrics with C.I. Acid Red 114 at 3% owf.

Resin/CC	K/S
<i>Wool (TF5400)</i>	
no resin/no CC	27.7
DMDHEU/CC	28.0
DMDHEU-G/CC	28.4
DHDMI/CC	28.4
<i>Cotton</i>	
no resin/no CC	3.99
DMDHEU/CC	25.3
DMDHEU-G/CC	26.4
DHDMI/CC	12.7
<i>Wool/Cotton</i>	
no resin/no CC	4.40
DMDHEU/CC	16.3
DMDHEU-G/CC	20.2
DHDMI/CC	21.6

From Tables 1,3, and 4, it is clear that these resin systems had no adverse effect on dye uptake of wool. In the case of cotton, all resin/CC pretreatments were effective for high K/S values. Note that in the case of DHDMI/CC, dye uptake on cotton was approximately half that of the other resin/CC systems. This can be attributed to the fewer number of reactive sites in DHDMI for attachment of both cellulose and CC.

Table 5 lists the results of colorfastness testing.

Table 5: Colorfastness of Wool/Cotton Pretreated with resins/CC before dyeing with C.I. Acid Red 114, 3% owf.

<u>Resin</u> CC*	Croaking		Dry Clean	Color Change	Stain	Light 20 hr
	wet	dry				
DMDHEU	3	4	5	5	1-2	2-3
DMDHEU-G	2-3	4-5	5	5	1	4
DHDMI	2-3	4-5	5	5	1	4

Colorfastness was determined according to the standard test methods listed for Table 2.

From Table 5, wash fastness stain was poor and would preclude home laundering. Thus the "dry clean only" label would be recommended. Light fastness for DMDHEU-G and DHDMI are acceptable as stipulated by ASTM D4155 specification requirements for "Women's and Girls Woven Sportswear, Shorts, Slacks, and Suiting Fabrics (13)."

Cold Batching

We examined previous reports on the various wet chemical modifications of cellulose for their potential to add amine or quaternary nitrogen groups to increase dyeability. We found it especially compelling that some modifications occurred on cellulose *in situ* with or without the presence of cellulose anion and by exhaust from solutions at room temperature. For example, when aminized cotton was treated further with ethyleneimine, there was improved ion-exchange character and dye uptake in a manner similar to wool (6,7).

Aminoalkylation was viewed as a route to improving the dyeing of cellulosic fibers, especially with direct dyes. Dyeing cotton with a direct dye is a reversible process and all the absorbed dye can be removed by prolonged washing. Certain commercially available cationic aftertreatments (fixatives), when applied by exhaustion from solution, have been recommended for improving colorfastness to washing. They are organic compounds of high molecular weights having cationic or amine functions and they contain ethylene polyamino chain extensions. They form salt linkages between the sulfonic acid solubilizing groups of the dye and the cationic compounds to produce less soluble dyes. The cationic fixative has affinity for the surface of the cellulose fiber and can act to bind the dye to the surface.

Some dye fixatives are fiber-reactive through epoxy, azetidinium, or guanidino groups incorporated into the ethylene polyamine structure. Epoxy-type or quaternary epoxy ammonium compounds are processed in alkaline medium for fixing onto cellulose by epoxide ring opening. They impart cationic charge for increased reactivity to dyes (14, 15). Azetidinium-type compounds include polyamide-epichlorohydrin resins (Hercosett 125) or resin with ethylenediamine. They improve the dyeability of cotton when applied at neutral pH. A simple azetidinium compound, 1,1-dimethyl-3-hydroxazetidinium chloride (DMAC), when applied at alkaline pH, has this same effect (16,17,18,19). Guanidino-type bases of high molecular weight have been known to act as mordants for the application of metachrome dyestuffs in the dyeing of wool/rayon blends, where first the rayon is pretreated with the polyamino derivative condensate (20.) Guanidine, the strongest organic base known, has a pK_a of 13.6 (21). Cellulose itself is weakly acidic, having a pK_a of approximately 13.7 (7). The weak acidity of cellulose may not provide the opportunity for nucleophilic reaction with the imine. The conversion to cellulose anion by sodium hydroxide may be required.

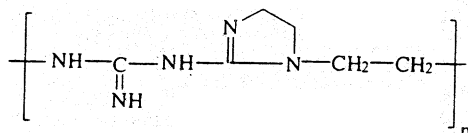
In this study, we have examined both nonreactive and reactive dye fixatives. They are described as follows:

Freetex 670 (Freedom), cationic, polyamino compound, designed to improve the washfastness of cellulosic textiles that have been dyed with direct, reactive, sulfur, and azo dyes. This compound is added to the last rinse in exhaust dyeing with pH adjusted to 5.0-5.5.

Solfix E (Ciba) - epoxy-type fiber-reactive polyamino chlorohydrin with quaternary ammonium functions; processed as aftertreatment with 30% sodium hydroxide.

Levogen FSE (Dystar), azetidinium-type cationic polyamino azetidine with quaternary nitrogen contained within a four-member strained ring. This compound can have marked reactivity toward the weak nucleophile, cellulose. Analogously, it has been reported that the weak nucleophile, methanol, is alkylated under mild conditions with ring opening (19).

Sandene 8425 Liquid (Clariant) ethylene polyamino cyanoguanidine with imidazoline function.



Product literature indicates that this is a specialty product for cationization through the chemical modification of cellulose. Pretreatment at pH 9.0 to 10.0 is recommended for cellulosic fibers (22). The effects of these dye fixatives on color strength and union shade are listed in Table 6.

Table 6: Effects of Commercial Dye Fixatives on the Dyeing of Wool, Cotton, and Wool/Cotton Union Cloth with C.I. Acid Red 114 at 3% owf.

C.I. Acid Red 114	
Dye Fixative	K/S
<i>Wool (TF530)</i>	
without fixative	27.73
Freetex	19.87
Solfix	24.58
Levogen	18.85
Sandene	23.41
<i>Cotton (400M)</i>	
without fixative	3.99
Freetex	15.36
Solfix	15.16
Levogen	14.72
Sandene	17.85
<i>Wool/Cotton (TF4504)</i>	
Freetex	15.01
Solfix	22.26
Levogen	15.56
Sandene	24.38

Colorfastness results are given below (Table 7).

Table 7: Colorfastness of Wool/Cotton Pretreated with Dye Fixatives and Dyed with C.I. Acid Red 114 at 3% owf.

Dye Fixatives	Crocking		Dry Clean	Color Change	Stain	Light 20 hr
	Wet	Dry				
Freetex	1	2	5	4-5	1	2-3
Solfix	1	2-3	5	5	1	2
Levogen	1	2	5	3	1	3
Sandene	1	2-3	5	4	1	2-3

From these results, Solfix E and Sandene 8425 Liquid perform the best as pretreatments for dyeing. They give high K/S values for wool and these values are nearly the same for wool/cotton. Cotton showed a dramatic increase in color strength as the results of all dye fixative pretreatments. However, because colorfastness was poor overall in Table 7, these dyed fabrics would be labeled, "dry clean only."

The effects of Sandene, Solfix, and Levogen pretreatments on color strengths and union shades of fabrics dyed with C.I. Direct Red 79 are shown in Tables 8 and 9.

Table 8: Effects of Commercial Dye Fixatives on the Dyeing of Wool, Cotton and Wool/Cotton Union Cloth, with C.I. Direct Red 79. at 3% owf.

C.I. Direct Red 79	
Dye Fixative	K/S
<i>Wool (TF530)</i>	
without fixative	27.47
Sandene	22.54
<i>Cotton (400M)</i>	
without fixative	3.59
Sandene	14.86
<i>Wool/Cotton (TF4504)</i>	
without fixative	10.51
Solfix	18.53
Levogen	16.01
Sandene	18.90

Colorfastness results are found in Table 9.

Table 9: Colorfastness of Wool, Cotton, and Wool/Cotton Pretreated with Dye Fixatives and Dyed with C.I. Direct Red 79 at 3% owf.

Dye Fixatives	Crocking Wet	Dry	Dry Clean	Color Change	Stain	Light 20 hr
Wool						
none	3-4	5	5	4	1-2	5
Sandene	1	3	5	4	1	5
Cotton						
Sandene	3	5	5	2	1	3-4
Wool/Cotton						
Solfix	2	4	4	5	1-2	4-5
Levogen	2	4-5	5	2-3	1	5
Sandene	1-2	4	5	2-3	1	4-5

As shown in Tables 8 and 9, in the case of C.I. Direct Red 79, Solfix and Sandene gave the highest K/S values for dyed wool/cotton. Note that the K/S the dyed wool fabric pretreated with Sandene is lower than that of unpretreated wool fabric. Also note that the K/S values for pretreated wool/cotton are lower than those of unpretreated wool. There appears to be a slight loss in color due to pretreatment. Although wool/cotton fabrics were dyed to union shades with C.I. Direct Red 79 after Solfix, Levogen, and Sandene pretreatments, colorfastness ratings for staining and wet crocking were poor as shown in Table 9. Thus care recommendation would be "dry clean only."

The best overall results were obtained when wool/cotton fabrics were pretreated with the guanidine-derived dye fixative, Sandene 8425 Liquid, followed by dyeings with wool reactive dyes. These results are shown in Tables 10 - 15.

Table 10: Effects of Guanidine Dye Fixative on the Dyeing of Wool, Cotton, and Wool/Cotton with C.I. Reactive Red 65 at 3% owf.

C.I. Reactive Red 65	
Dye Fixative	K/S
<i>Wool (TF530)</i>	
without fixative	23.59
Sandene	23.87
<i>Cotton (400M)</i>	
without fixative	0.67
Sandene	13.50
<i>Wool/Cotton (TF4504)</i>	
without fixative	3.36
Sandene	18.96

Colorfastness results are found in Table 11.

Table 11: Colorfastness of Wool, Cotton, and Wool/Cotton Pretreated with Guanidine Dye Fixative and Dyed with C.I. Reactive Red 65 at 3% owf.

Dye Fixatives	Crocking		Dry Clean	Color Change	Stain	Light 20 hr
	Wet	Dry				
Wool						
none	2-3	3-4	5	5	2	5
Sandene	3	4	5	5	2	5
Cotton						
Snadene	3	5	5	5	2	3-4
Wool/Cotton						
Sandene	2-3	4	5	4-5	2	5

As was observed with C.I. Acid Red 114 and C.I. Direct Red 79, C.I. Reactive Red 65 had a color diminishing effect on pretreated wool/cotton when compared to unpretreated wool. Unlike the results of dyeing with C.I. Direct Red 79, pretreated wool/cotton fabrics dyed with C.I. Reactive Red 65 exhibited nearly the same K/S values for wool with and without Sandene pretreatment (Table 10). Note in Table 11 that the colorfastness properties of wool/cotton fabrics dyed with C.I. Reactive Red 65 showed improvement in colorfastness when compared to those dyed with C.I. Direct Red 79 in Table 9.

The values for K/S and the colorfastness ratings of fabrics pretreated with guanidine dye fixative followed by dyeing with C.I. Reactive Blue 69 are shown in Tables 12 and 13.

Table 12: Effects Guanidine Dye Fixative on the Dyeing of Wool, Cotton, and Wool/Cotton with C.I. Reactive Blue 69 at 3% owf.

C.I. Reactive Blue 69	
Dye Fixative	K/S
<i>Wool (TF530)</i>	
without fixative	26.69
Sandene	25.55
<i>Cotton (400M)</i>	
without fixative	0.56
Sandene	10.14
<i>Wool/Cotton</i>	
without fixative	2.49
Sandene	15.77

Colorfastness results are found in Table 13.

Table 13: Colorfastness of Wool, Cotton, and Wool/Cotton Pretreated with Guanidine Dye Fixative and Dyed with C.I. Reactive Blue 69 at 3% owf.

Dye Fixatives	Crocking		Dry Clean	Color Change	Stain	Light 20 hr
	wet	dry				
Wool						
none	3-4	5	5	4	5	5
Sandene	3	4-5	5	4-5	5	5
Cotton						
Sandene	3-4	5	5	4-5	4	5
Wool/Cotton						
Sandene	3	4-5	4-5	5	5	5

Pretreatment with these dye fixatives followed by dyeing with C.I. Reactive Blue 69 also caused a slight diminishing effect of shade on dyed wool/cotton fabrics when these fabrics are compared to unpretreated wool dyed with the same dye. In the case of C.I. Reactive Blue 69, the results in Table 13 show that colorfastness properties were improved sufficiently so that these fabrics could be recommended for home laundering.

The values for K/S and colorfastness of fabrics pretreated with Guanidine Dye Fixative and dyed with C.I. Reactive Yellow 39 are shown in Tables 14 and 15.

Table 14: Effects Guanidine Dye Fixative on the Dyeing of Wool, Cotton, and Wool/Cotton with C.I. Reactive Yellow 39 at 3% owf.

C.I. Reactive Yellow 39	
Dye Fixative	K/S
<i>Wool (TF530)</i>	
without pretreatment	24.08
Sandene	25.47
<i>Cotton (400M)</i>	
without pretreatment	0.57
Sandene	11.45
<i>Wool/Cotton</i>	
without pretreatment	2.90
Sandene	18.12

Colorfastness results are found in Table 15.

Table 15: Colorfastness of Wool, Cotton, and Wool/Cotton Pretreated with Guanidine Dye Fixative and Dyed with C.I. Reactive Yellow 39 at 3% owf.

Dye Fixatives	Crocking		Dry Clean	Color Change	Stain	Light 20 hr
	wet	dry				
Wool						
none	4	5	5	5	5	5
Sandene	4	4-5	5	5	5	5
Cotton						
Sandene	4-5	5	5	5	5	3
Wool/Cotton						
Sandene	3-4	5	5	5	5	4-5

In summary, pretreated fabrics dyed with C.I. Reactive Blue 69 and C.I. Reactive Yellow 39 showed improved colorfastness properties when compared to C.I. Acid Red 114, C.I. Direct Red 79, and C.I. Reactive Red 65.

Conclusion

The pretreatment systems examined in these studies have been known to improve the properties of wool to a lesser extent than cotton. Polyamine pretreatments are appropriate for cellulose because of the large number of reactive sites relative to wool. Although wool has amino, hydroxyl, and thiol reactive sites, it lacks cellulose's wide range of reactivity for structural modification. Thus, relative to cellulose, the polyamization of wool is relatively limited. Yet, epoxy compounds have been used to control the dimensional stability of wool. Polyamino azetidinium compounds are well known for imparting dimensional stability to wool. Polyamino guanidine compounds have been used to modify rayon in wool/rayon blends for dyeability similar to wool.

We have found that none of the pretreatments increased the dyeability of wool, thus a retarding agent was not necessary to achieve union shades. We have demonstrated the feasibility of using certain dye fixatives as pretreatment systems for union dyeing wool/cotton fabrics in one dyebath with wool-reactive dyes. The dye can be processed at nearly neutral pH to circumvent selective dye absorption by the wool. The wool reactive dyes require no alkali so the conditions favor wool. Our past results showed that these pretreatments and pretreatment conditions have no negative effects on wool.

When resin/amine is compared to resin/CC pretreatments, the colorfastness of the resin/amine system is superior and unsurpassed by any of the dye fixative pretreatments. In the case of pretreatment with dye fixative, C.I. Acid Red 114 dye is not recommended but other acid dyes with better colorfastness properties should be examined. Solfix E and Levogen FSE can be used to pretreat wool/cotton for union dyeing with C.I. Direct Red 79 provided dry cleaning is used to refurbish these fabrics. Sandene 8425 Liquid pretreatment proved to be superior as a pretreatment to dyeing wool/cotton textiles to union shades with the wool reactive dyes: C.I. Reactive Blue 69 and C.I. Reactive Yellow 39. Another wool reactive dye should be investigated similarly. It is reasonable to assume that other wool reactive dyes can be selected to give equally improved colorfastness properties provided union shades are obtained. From this work, pretreatment with the guanidine-derived fixative can be recommended for union dyeing wool/cotton with bromoacrylamido-type wool reactive dyes. These pretreatment/dye systems offer improved colorfastness and easy processing of wool/cotton union shades.

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